

The Osmotic Pressure of Cane Sugar Solutions at 10°.

DISSERTATION

SUBMITTED TO THE BOARD OF GRADUATE STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

HARMON V. MORSE.

1908

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
1908

The Osmotic Pressure of Cane Sugar Solutions at 10°.

DISSERTATION

SUBMITTED TO THE BOARD OF GRADUATE STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.



BY

HARMON V. MORSE.

1908

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
1908

CONTENTS.

Acknowledgment.....	4
Introduction.....	5
Sources of Error.....	6
I. Thermometer Effects.....	7
II. Displacement of the Manometer.....	7
III. Dilution of the Cell Contents.....	8
Series I.....	10
Record of Experiments.....	11
Summary of Results.....	17
Discussion of Results.....	19
Series II.....	21
Record of Experiments.....	23
Summary of Results.....	33
Discussion of Results.....	35
Concordance of Results.....	38
Molecular Ratios.....	38
Temperature Coefficient.....	39
Biography.....	42

ACKNOWLEDGMENT.

The writer wishes to express his appreciation of the instruction received in the laboratory and lecture room from President Remsen, Professor Morse, Professor Jones, Professor Renouf, Professor Clarke, Associate-Professor Acree, Dr. Tingle and Associate-Professor Swartz.

Especially does he appreciate the careful and thorough training received with Professor Morse, under whom this investigation has been pursued.

The Osmotic Pressure of Cane Sugar Solutions at 10°.

INTRODUCTION.

Determinations of the osmotic pressures of cane sugar solutions in the vicinity of 0°,¹ 4°,² and 20°³ have been carried out in the past few years in this laboratory by H. N. Morse and his co-workers which have developed the following facts:

I. The pressures obtained at the two limiting temperatures thus far investigated, *i. e.*, at 0° and at 20° vary only slightly.

II. At the intermediate temperature, 4°, the osmotic pressure is practically the same as at 0° and at 20°.

It was stated regarding the series at 0°: "Others may discover in the high pressures in question, and in the fact that they are, in a general way, nearly equal to those which were obtained in the vicinity of 20°, a suggestion that osmotic pressure, unlike that of gases, *has little or no* temperature coefficient. But an equally just suspicion, apparently, is that somewhere between 0° and 20° a temperature may be found at which osmotic pressure, like the volume of the solvent, is at a minimum, and from which it increases, with change of temperature in both directions."⁴

No minimum having been found in the vicinity of 4°, two other intermediate temperatures, namely, 10° and 15°⁵, were selected in order to ascertain whether, at either of these, there might be a minimum in osmotic pressure, also for the purpose of throwing more light on the question of the deviation of osmotic from gas pressure, *i. e.*, upon

¹ Am. Chem. J., **37**, 425.

² *Ibid.*, **38**, 175.

³ *Ibid.*, **36**, 39.

⁴ *Ibid.*, J., **37**, 466.

⁵ *Ibid.*, **40**,

the question of the temperature coefficient of osmotic pressure.

As a result of the work at 10° , two series of measurements are given in this dissertation. The first of these was carried out in the Spring of 1907 under the same general conditions as in the previous measurements in the vicinity of 0° and 4° . Consequently, they are subject in some degree to the uncertainties regarding the actual magnitude of the osmotic pressures which have been pointed out from time to time in connection with the earlier work.

It has been customary to make duplicate determinations of the osmotic pressure of ten concentrations of the solution ranging between 0.1 and 1.0 weight-normal. In this respect, Series I. is incomplete because, while the work was in progress, important improvements in the method were introduced which made it desirable to repeat the whole work under the more advantageous conditions. Nevertheless, the results obtained in the earlier work are given as having some value in connection with the general problem of osmotic pressure.

The measurements given in Series II. were all made under the improved conditions referred to above.

In order to make clear the character of the improvements in method which were introduced and which made a repetition of the earlier measurements desirable, there is introduced here a brief statement of the sources of error which had been encountered in the determination of osmotic pressure.

SOURCES OF ERROR.

The larger sources of error which have been encountered in the attempt to measure osmotic pressure are: (1) "thermometer effects;" (2) upward displacement of the manometer while in the closed cell, with more or less distortion of the rubber stopper; (3) the dilution of the cell contents.

The minor source of error which may be mentioned in this connection was the slow diminution of the air volume in the manometer.

(1) *Thermometer Effects.*

When the temperature of the bath rises, the solution within the cell expands more rapidly, and to a greater extent, than the cell itself. This expansion of the liquid causes water to be expelled from the solution through the membrane and is attended by a concentration of the solution. If the passage of the water through the membrane is not sufficiently rapid, as it usually is not, there is created an abnormally high pressure which, if the rise in temperature is rapid, may considerably exceed the true osmotic pressure of the solution.

On the other hand, if the temperature of the bath falls, the solution contracts more rapidly than the containing cell, and water passes through the membrane in the reverse direction. If this passage from the outer vessel to the solution within the cell is not rapid enough to neutralize the shrinkage of the solution, there is established an abnormally low pressure.

In the first series of measurements of osmotic pressure the thermometer effects were large and the results were correspondingly inexact.

The methods of maintaining comparatively constant temperatures in the bath were, however, improved as the work progressed until, when the investigation in Series II. was undertaken, it was practicable to maintain, throughout a measurement of pressure, temperatures which did not vary more than 0.2° .

(2) *Displacement of the Manometer and Distortion of the Rubber Stopper.*

The upward displacement of the manometer under pressure, with the accompanying distortion of the rubber stopper which holds the manometer and closes the cell, is attended by an increase in the capacity of the cell and a corresponding dilution of the solution. The first two series of measurements of the osmotic pressure of cane sugar solutions, *i. e.*, in the vicinity of 20° ,¹ also the first series of measurements

¹ Am. Chem. J., **36**, 50; **37**, 328, 460.

of glucose solutions,¹ were considerably affected by this source of dilution, but in the succeeding series effective measures were devised for rendering the stoppers so rigid in their places, that the upward movements of the manometers became quite insignificant.

In the present work—Series II.—the greatest displacement of the manometer during a measurement was 1.29 mm. while the average displacement amounted to only 0.3 mm.

(3) *Dilution of the Cell Contents.*

One source of dilution in the cell contents has been mentioned above. This would have been of little importance if it had been the only source of dilution because it is known to precede the measurement of pressure and can be corrected for, if uncomplicated with dilution which is subsequent to the measurement of pressure.

There is, however, another source of dilution in the water which fills the cell wall² at the time of closing and opening the cell. If the contents of the cell are at any time during these operations under diminished pressure, the water is sucked in from the porous wall through the membrane, and the solution is diluted. The dilution due to this cause, which occurs while the cell is being closed, precedes the measurement of pressure, and a correction should be made for it; but the dilution due to diminished pressure, which occurs while the cell is being opened, is subsequent to the measurement and must be neglected.

Unfortunately, there was no possibility of ascertaining how much of the total observed dilution occurred at either of these periods. In other words, it was not practicable to determine how much of the total dilution should be corrected for, and how much should be neglected.

A partial remedy for dilution due to the sucking in of water from the cell wall, while closing and opening the cell, was found in the process of dipping³ the cell, after filling

¹ Am. Chem. J., **36**, 23.

² *Ibid.*, **36**, 26, 49; **37**, 589.

³ *Ibid.*, **37**, 464, 584.

with the solution, in another solution of equal or somewhat greater concentration; also in a more rapid and careful manipulation. The improvement effected in this way is to be seen in the diminishing "total dilution" in the succeeding series of measurements of the osmotic pressure of cane sugar solutions.

In the first series in which the polariscope was used—that in the vicinity of 20° ¹—the average amount of dilution was 2.8 per cent. In the second—that at 0° ²—it was 1.47 per cent, while in the third—that at 4° ³—it was 1.28 per cent.

The proper distribution of this dilution in the correction of the results has been much discussed⁴ in the various papers on osmotic pressure which have appeared from this laboratory.

It was concluded that not less than half of the total dilution must occur while the cells are being opened, because, during that period, the contents are, for a longer time, and more continuously, subjected to diminished pressure than while the cells are being closed. The plan was, therefore, adopted for a time of correcting the results for only one-half of the observed dilution. Later, when a cell was to be opened, the stopper was pierced by a hypodermic needle which brought the cell contents at once under atmospheric pressure and prevented any diminution of that pressure during the removal of the stopper and, consequently, any dilution of the solution.

It was found after introducing this modification of earlier practice that there was very little, and frequently no, dilution whatever of the cell contents. In the majority of cases the solutions when removed from the cells exhibited the same rotation as the original solutions, showing that in neglecting one half of the loss in rotation, the results of earlier series had been overcorrected rather than undercorrected for dilution.

¹ Am. Chem. J., **36**, 39.

² *Ibid.*, **37**, 425.

³ *Ibid.*, **38**, 175.

⁴ *Ibid.*, **34**, 30, 92; **36**, 40, 48; **37**, 427, 461; **38**, 177, 199.

It was this elimination of practically all the dilution of the cell contents which caused the writer to undertake Series II. of the measurements presented in this dissertation.

SERIES I.

As has been stated, the measurements belonging to this Series were carried out during April and May, 1907, before methods were devised for the suppression of practically all dilution and for the exact control of temperature conditions. At the same time they are as accurate as those determinations in the vicinity of 4° and agree with the general relations of osmotic to gas pressure established in the earlier work.

The pressures of two of the concentrations—the 0.8 and 0.9 normal—were not measured, time not permitting. Nor were duplicate measurements made in the majority of cases for the same reason.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $12^{\circ}.6$; (2) at conclusion of Exp., $12^{\circ}.6$; loss, $0^{\circ}=0$ per cent. *Manometer*: No. 13; volume of air, 435.09; displacement, 0.02 mm. Cell used, D. Resistance of membrane, 550,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.48; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.99. Time of setting up cell, 4.30 P.M., Apr. 20, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 21.						
2.30 P.M.	$9^{\circ}.4$	$10^{\circ}.0$	148.24	2.43	2.30	0.13
8.00 P.M.	$9^{\circ}.5$	$10^{\circ}.25$	148.07	2.44	2.30	0.14
April 22.						
8.30 A.M.	$9^{\circ}.6$	$10^{\circ}.3$	148.14	2.44	2.31	0.13
				2.44	2.30	0.14

Molecular osmotic pressure, 24.40.

Molecular gas pressure, 23.03.

Ratio of osmotic to gas pressure, 1.059.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $12^{\circ}.6$; (2) at conclusion of Exp., $12^{\circ}.5$; loss, $0^{\circ}.1=0.79$ per cent. *Manometer*: No. 11; volume of air, 465.94; displacement, 0.02 mm. Cell used, B. Resistance of membrane, 550,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.40; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.89. Time of setting up cell, 4.30 P.M., Apr. 20, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 21.						
2.30 P.M.	$9^{\circ}.4$	$10^{\circ}.0$	154.68	2.42	2.30	0.12
8.00 P.M.	$9^{\circ}.5$	$10^{\circ}.25$	154.54	2.43	2.30	0.13
April 22.						
9.00 P.M.	$9^{\circ}.7$	$10^{\circ}.4$	153.92	2.44	2.31	0.13
				2.43	2.30	0.13

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.30.

Molecular gas pressure, 23.03.

Ratio of osmotic to gas pressure, 1.055.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $24^{\circ}.9$; (2) at conclusion of Exp., $24^{\circ}.7$; loss, $0^{\circ}.2 = 0.8$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.3 mm. Cell used, H. Resistance of membrane, 280,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.47; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.81. Time of setting up cell, 4.00 P.M., Apr. 22, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 22. 8.00 P. M.	$10^{\circ}.2$	$10^{\circ}.2$	89.78	4.78	4.62	0.16
April 23. 8.30 A.M.	$10^{\circ}.0$	$10^{\circ}.8$	89.97	4.78	4.62	0.16
2.00 P.M.	$9^{\circ}.9$	$10^{\circ}.8$	90.19	4.77	4.61	0.16
				4.78	4.62	0.16

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.90.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.035.

Table IV.

0.3 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $36^{\circ}.6$; (2) at conclusion of Exp., $36^{\circ}.25$; loss, $0^{\circ}.35 = 0.96$ per cent. *Manometer*: No. 11; volume of air, 465.94; displacement, 0.4 mm. Cell used, B. Resistance of membrane, 276,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.53; (3) dilution, 0.05; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 6.10. Time of setting up cell, 4.00 P.M., Apr. 23, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 24. 8.00 A.M.	$10^{\circ}.2$	$11^{\circ}.0$	61.00	7.15	6.93	0.22
2.00 P.M.	$10^{\circ}.1$	$11^{\circ}.0$	60.93	7.16	6.93	0.23
5.00 P.M.	$10^{\circ}.2$	$11^{\circ}.2$	61.03	7.14	6.93	0.21
				7.15	6.93	0.22

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.87.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.032.

Table V.

0.3 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $36^{\circ}.6$; (2) at conclusion of Exp., $36^{\circ}.4$; loss, $0^{\circ}.2 = 0.55$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.34 mm. Cell used, B. Resistance of membrane, 183,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.50; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.67. Time of setting up cell, 5.00 P.M., Apr. 11, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 12. 9.00 P.M.	$10^{\circ}.0$	$11^{\circ}.0$	62.22	7.18	6.92	0.26
April 13. 9.00 P.M.	$9^{\circ}.4$	$10^{\circ}.0$	62.17	7.18	6.91	0.27
April 14. 4.00 P.M.	$9^{\circ}.2$	$10^{\circ}.0$	62.02	7.19	6.91	0.28
				7.18	6.92	0.27

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.94.

Molecular gas pressure, 23.04.

Ratio of osmotic to gas pressure, 1.038.

Table VI.

0.4 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $48^{\circ}.0$; (2) at conclusion of Exp., $47^{\circ}.6$; loss $0^{\circ}.4 = 0.83$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.05 mm. Cell used, G. Resistance of membrane, 158,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.40. Time of setting up cell, 4.00 P.M., Apr. 17, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 18. 8.30 A.M.	$9^{\circ}.3$	$10^{\circ}.4$	47.82	9.47	9.21	0.26
2.00 P.M.	$9^{\circ}.6$	$10^{\circ}.5$	47.74	9.47	9.22	0.25
5.00 P.M.	$9^{\circ}.6$	$10^{\circ}.65$	47.81	9.47	9.22	0.25
				9.47	9.22	0.25

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.68.

Molecular gas pressure, 23.04.

Ratio of osmotic to gas pressure, 1.027.

Table VII.

0.5 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $58^{\circ}.9$; (2) at conclusion of Exp., $58^{\circ}.2$; loss, $0^{\circ}.7 = 1.19$ per cent. *Manometer*: No. 21; volume of air, 477.75; displacement, 0.01 mm. Cell used, O. Resistance of membrane, 278,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.53; (3) dilution, 0.10; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.66. Time of setting up cell, 4.00 P.M., Apr. 9, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 10.						
11.00 A.M.	$9^{\circ}.85$	$10^{\circ}.2$	38.85	11.90	11.54	0.36
4.00 P.M.	$9^{\circ}.6$	$10^{\circ}.7$	38.88	11.89	11.53	0.36
April 11.						
8.00 A.M.	$9^{\circ}.8$	$10^{\circ}.3$	38.82	11.90	11.53	0.37
				11.90	11.53	0.36

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.79.

Molecular gas pressure, 23.07.

Ratio of osmotic to gas pressure, 1.032.

Table VIII.

0.5 Wt. normal solution. Exp. No. 2. *Rotation*: (1) original, $58^{\circ}.9$; (2) at conclusion of Exp., $58^{\circ}.1$; loss, $0^{\circ}.8 = 1.36$ per cent. *Manometer*: No. 6; volume of air, 396.89; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 183,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.66; (3) dilution, 0.12; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.02. Time of setting up cell, 4.00 P.M., Apr. 8, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 9.						
9.00 P.M.	$10^{\circ}.2$	$11^{\circ}.2$	32.21	11.91	11.55	0.36
April 10.						
9.00 A.M.	$10^{\circ}.0$	$10^{\circ}.5$	32.28	11.89	11.54	0.35
1.00 P.M.	$9^{\circ}.6$	$10^{\circ}.3$	32.30	11.88	11.53	0.35
				11.89	11.54	0.35

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.79.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.031.

Table IX.

0.5 Wt. normal solution. Exp. No. 3. *Rotation*: (1) original, $58^{\circ}.9$; (2) at conclusion of Exp., $58^{\circ}.4$; loss, $0^{\circ}.5 = 0.85$ per cent. *Manometer*: No. 5; volume of air, 434.98; displacement, 0.04 mm. Cell used, D. Resistance of membrane, 275,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.64; (3) dilution, 0.07; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.98. Time of setting up cell, 4.00 P.M., Apr. 8, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 9.						
9.00 P.M.	$10^{\circ}.2$	$11^{\circ}.2$	35.08	12.02	11.55	0.47
April 10.						
11.00 A.M.	$9^{\circ}.85$	$10^{\circ}.2$	35.14	11.99	11.54	0.45
4.00 P.M.	$9^{\circ}.6$	$10^{\circ}.45$	35.17	11.98	11.53	0.45
				12.00	11.54	0.46

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.99.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.040.

Table X.

0.6 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $69^{\circ}.4$; (2) at conclusion of Exp., $68^{\circ}.6$; loss, $0^{\circ}.8 = 1.15$ per cent. *Manometer*: No. 6; volume of air, 396.89; displacement, 0.05 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.65; (3) dilution, 0.07; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, —. Time of setting up cell, 4.00 P.M., Apr. 11, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 12.						
10.00 A.M.	$10^{\circ}.0$	$10^{\circ}.4$	26.78	14.39	13.85	0.54
1.00 P.M.	$9^{\circ}.8$	$10^{\circ}.5$	26.81	14.37	13.84	0.53
5.00 P.M.	$9^{\circ}.7$	$10^{\circ}.4$	26.79	14.39	13.83	0.56
				14.38	13.84	0.54

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 23.97.

Molecular gas pressure, 23.07.

Ratio of osmotic to gas pressure, 1.039.

Table XI.

0.7 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, 79.3 ; (2) at conclusion of Exp., $78^{\circ}.3$; loss, $1^{\circ} = 1.26$ per cent. *Manometer*: No. 21; volume of air, 477.75 ; displacement, 0.11 mm. Cell used, D. Resistance of membrane, $370,000$. *Corrections*: (1) atmospheric pressure, 1.00 ; (2) liquids in manometer, 0.55 ; (3) dilution, 0.15 ; (4) concentration, 0 ; (5) capillary depression, 0.02 . Initial pressure, 13.92 . Time of setting up cell, 4.00 P.M., Apr. 25, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
April 25. 8.30 P.M.	$11^{\circ}.2$	$12^{\circ}.35$	27.19	17.00	16.23	0.77
April 26. 2.00 P.M.	$11^{\circ}.2$	$12^{\circ}.25$	27.15	17.03	16.23	0.80
April 27. 11.00 A.M.	$11^{\circ}.8$	$12^{\circ}.4$	27.03	17.04	16.26	0.78
				17.04	16.24	0.78

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.32 .

Molecular gas pressure, 23.20 .

Ratio of osmotic to gas pressure, 1.048 .

Table XII.

1.0 Wt. normal solution. Exp. No. 1. *Rotation*: (1) original, $107^{\circ}.6$; (2) at conclusion of Exp., $106^{\circ}.4$; loss, $1^{\circ}.2 = 1.12$ per cent. *Manometer*: No. 13; volume of air, 435.09 ; displacement, 0.03 mm. Cell used, D. Resistance of membrane, $220,000$. *Corrections*: (1) atmospheric pressure, 1.00 ; (2) liquids in manometer, 0.66 ; (3) dilution, 0.19 ; (4) concentration, 0 ; (5) capillary depression, 0.02 . Initial pressure, 19.92 . Time of setting up cell, 4.00 P.M., May 1, 1907.

Time.	Temperature.		Volume air.	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
May 1. 5.00 P.M.	$10^{\circ}.5$	$11^{\circ}.4$	17.10	24.93	23.12	1.81
May 2. 11.30 A.M.	$9^{\circ}.8$	$11^{\circ}.2$	17.10	24.94	23.07	1.87
9.00 P.M.	$9^{\circ}.4$	$10^{\circ}.65$	17.16	24.86	23.03	1.83
				24.91	23.07	1.84

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.91 .

Molecular gas pressure, 23.07 .

Ratio of osmotic to gas pressure, 1.080 .

Table XIII. Series I.
Summary of Results.

Weight-normal concentration.	No. of experiment.	Temperature of solution.	Percent loss in rotation.	Osmotic pressure.			Theoretical gas pressure.
				Inversion.	One half dilution.	No inversion, no dilution.	
0.1	1	9°.5	0.00	2.44	2.44	2.44	2.30
0.1	2	9°.5	0.79	2.43	2.45	2.44	2.30
0.2	1	10°.0	0.80	4.78	4.83	4.80	4.62
0.3	1	10°.2	0.96	7.15	7.23	7.20	6.93
0.3	2	9°.5	0.55	7.18	7.23	7.21	6.92
0.4	1	9°.5	0.83	9.47	9.57	9.53	9.22
0.5	1	9°.8	1.19	11.90	12.07	12.00	11.53
0.5	2	9°.9	1.36	11.89	12.09	12.01	11.54
0.5	3	9°.9	0.85	12.00	12.12	12.07	11.54
0.6	1	9°.8	1.15	14.38	14.58	14.50	13.84
0.7	1	11°.4	1.26	17.02	17.28	17.17	16.24
1.0	1	9°.9	1.12	24.91	25.24	25.10	23.07

Table XIV. Series I.

Summary of Results.—Mean Values.

Weight-normal concentration.	Temperature of solution.	Per cent loss in rotation.	Osmotic pressures.			Theoretical gas pressure.
			Inversion.	One half dilution.	No inversion, no dilution.	
0.1	9°.5	0.40	2.44	2.45	2.44	2.30
0.2	10°.0	0.80	4.78	4.83	4.80	4.62
0.3	9°.9	0.76	7.17	7.23	7.21	6.93
0.4	9°.5	0.83	9.47	9.57	9.53	9.22
0.5	9°.9	1.13	11.93	12.09	12.03	11.54
0.6	9°.8	1.15	14.38	14.58	14.50	13.84
0.7	11°.4	1.26	17.02	17.28	17.17	16.24
1.0	9°.9	1.12	24.91	25.24	24.10	23.07

Av. = 10°.0 Av. = 0.93

The essential data of the individual measurements are given in Tables I. to XII., inclusive, and are summarized in Table XIII. They reappear as mean values for each concentration in Table XIV.

The wide variation in temperature as compared with the next series will be seen by referring to Table XIV. Though the average temperature for the series was 10° , it will be noticed that the mean temperatures for the individual concentrations varied from $9^{\circ}.5$ in the 0.1 and 0.4 normal to $11^{\circ}.4$ in the 0.7 normal.

That little dilution could have taken place from slipping of the manometers, is seen in Table I. to XII., inclusive. The largest displacement was 0.4 mm. in case of the 0.3 normal, while the average displacement was only 0.12 mm.

The average loss in rotation given in Table XIV. was 0.93 per cent. This was a marked improvement on the losses in previous series of the osmotic pressures of cane sugar solutions. The average losses in rotation in the three former series were as follows:

Series.	Temperature.	Loss, per cent.
II.	20°	2.8 ¹
III.	0°	1.47 ²
IV.	4°	1.28 ³
This series.	10°	.93

In Tables I. to XII., inclusive, the loss in rotation was corrected as being due wholly to inversion. Even at this time, however, such correction was believed to give too low results. Consequently, the results were also corrected by ascribing one half the loss in rotation to dilution. The reason for such correction has been fully explained in connection with earlier work.¹ The pressures, as corrected for half dilution, are given in Table XIII., and the mean results in Table XIV.

The pressures, as they would be without correction, either for inversion or for dilution, *i. e.*, the actually observed

¹ Am. Chem. J., **38**, 39.

² *Ibid.*, **37**, 457.

³ *Ibid.*, **38**, 178.

⁴ *Ibid.*, **37**, 463.

osmotic pressures, will likewise be noticed in Tables XIII. and XIV. These two columns are based on the fact, recently discovered, that practically *all the dilution* has heretofore taken place while the cell was being opened and is, therefore, subsequent to the measurement of osmotic pressure. It is evident that such dilution should be excluded in any correction of the observed pressures.

The experimental proof on which this fact is based, and which is of such a nature as to leave little doubt that the *actually observed osmotic pressure* is an extremely close approximation to the true pressure, will be given in the discussion of the results obtained in Series II.

Table XV. shows the differences between the osmotic pressures calculated in the three different ways just mentioned and the gas pressures for the corresponding concentrations and temperatures.

Table XV.—Differences between Osmotic and Gas Pressure.
Series I.

Weight-normal concentration.	If all loss in rotation is ascribed to inversion.	If one half the loss in rotation is ascribed to dilution.	If all loss in rotation is ascribed to subsequent dilution.
0.1	0.14	0.15	0.14
0.2	0.16	0.21	0.18
0.3	0.24	0.30	0.28
0.4	0.25	0.35	0.31
0.5	0.39	0.55	0.49
0.6	0.54	0.74	0.66
0.7	0.78	1.04	0.93
1.0	1.84	2.17	2.03

In Table XVI. are given the ratios of the molecular osmotic pressures to the molecular gas pressures likewise based upon the three different methods of correction.

Table XVI.—*Ratios of Molecular Osmotic to Molecular Gas Pressure.*

Series I.

Weight-normal concentration.	If all loss in rotation is ascribed to inversion.	If one half the loss in rotation is ascribed to dilution.	If all loss in rotation is ascribed to subsequent dilution.
0.1	1.057	1.061	1.059
0.2	1.035	1.045	1.040
0.3	1.035	1.045	1.040
0.4	1.027	1.038	1.033
0.5	1.034	1.049	1.042
0.6	1.039	1.053	1.046
0.7	1.048	1.069	1.059
1.0	1.080	1.094	1.087

A minimum in the ratios will be noticed in the 0.4 normal. A similar minimum was observed in the case of the 0.4 normal¹ at 0°, but at 4° the minimum appeared to occur in the 0.3 normal.²

SERIES II.

Effective methods having been devised for overcoming the dilution in the cell and for greatly reducing the "thermometer effects," it seemed desirable to redetermine the osmotic pressure of cane sugar solutions at 10°. The results of such a redetermination are given in the following tables.

During the entire two months over which this series of measurements extended, the maximum fluctuation in the temperature of the bath was only 0°.4. The fluctuation in consecutive readings, however, which is the thing to be guarded against, in only two cases was as high as 0°.2, while the average fluctuation in temperature was less than 0°.1. Consequently, temperature effects were practically eliminated in Series II.

The average displacement of the manometers was 0.3 mm. This displacement was too small to cause any sensible dilution and, consequently, any loss in rotation.

The third, and chief cause of uncertainty regarding the

¹ Am. Chem. J., 38, 207.

² *Ibid.*, 38, 207.

correct osmotic pressures, was satisfactorily solved by the use of the hypodermic needle in opening the cell.

The manometers used in this series were filled with nitrogen instead of air. It had been found in the course of earlier work that in manometers filled with air there is a slow and continuous diminution in the volume of the gas, notwithstanding the extreme care with which the mercury had been prepared.

This loss may be due to two causes—either to the action of the oxygen of the air on the mercury itself or on any traces of amalgam present, or to the stretching of the manometer tube under pressure. The question of this stretching under pressure is now under investigation in this laboratory.

The solutions were, of course, made up on the weight-normal basis and the sugar used was the purest obtainable rock candy. Two analyses made in this laboratory gave

Carbon.		
	Found, per cent.	Theoretical, per cent.
I	42.02	42.08
2	42.08	...

Hydrogen.		
	Found, per cent.	Theoretical, per cent.
I	6.42	6.48
2	6.47	...

Tables I. to XX., inclusive, present the essential data of the individual determinations. These are summarized in Table XXI. Table XXII. contains the mean values for each concentration of solution.

Table I.

0.1 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $12^{\circ}.8$; (2) at conclusion of Exp., $12^{\circ}.8$; loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.08 mm. Cell used, H. Resistance of membrane, 136,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.46; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 1.97. Time of setting up cell, 4.00 P.M., March 2, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 5.						
11.45 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	147.12	2.42	2.31	0.11
March 6.						
10.30 A.M.	$10^{\circ}.0$	$10^{\circ}.7$	146.78	2.43	2.31	0.12
				2.43	2.31	0.12

Molecular osmotic pressure, 24.25.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.050.

Table II.

0.1 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $12^{\circ}.8$; (2) at conclusion of Exp., $12^{\circ}.8$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 219,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.69. Time of setting up cell, 3.30 P.M., March 2, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 5.						
8.40 A.M.	$10^{\circ}.0$	$10^{\circ}.3$	136.68	2.43	2.31	0.12
11.15 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	136.17	2.45	2.31	0.14
March 6.						
10.30 A.M.	$10^{\circ}.0$	$10^{\circ}.7$	136.28	2.44	2.31	0.13
				2.44	2.31	0.13

Molecular osmotic pressure, 24.40.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.056.

Table III.

0.2 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $25^{\circ}.0$; (2) at conclusion of Exp., $25^{\circ}.0$; loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.09 mm. Cell used, G. Resistance of membrane, 283,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.56; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.66. Time of setting up cell, 11.30 A.M., January 21, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	$10^{\circ}.2$	$10^{\circ}.8$	82.91	4.80	4.62	0.18
8.10 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	82.87	4.80	4.62	0.18
Jan. 23.						
10.00 A.M.	$10^{\circ}.0$	$10^{\circ}.7$	82.37	4.83	4.62	0.21
				4.81	4.62	0.19

Molecular osmotic pressure, 24.05.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.041.

Table IV.

0.2 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $25^{\circ}.0$; (2) at conclusion of Exp., $25^{\circ}.0$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 141,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.78. Time of setting up cell, 11.30 A.M., January 21, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 22.						
11.40 A.M.	$10^{\circ}.2$	$10^{\circ}.8$	76.98	4.82	4.62	0.20
8.10 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	76.98	4.82	4.62	0.20
10.30 P.M.	$10^{\circ}.0$	$10^{\circ}.8$	76.84	4.83	4.62	0.21
Jan. 23.						
10.00 A.M.	$10^{\circ}.0$	$10^{\circ}.7$	76.62	4.85	4.62	0.23
				4.83	4.62	0.21

Molecular osmotic pressure, 24.15.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.045.

Table V.

0.3 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $36^{\circ}.6$; (2) at conclusion of Exp., $36^{\circ}.6$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.02 mm. Cell used, G. Resistance of membrane, 158,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.00. Time of setting up cell, 5.00 P.M., March 12, 1908.

Time,	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 13.						
10.30 P.M.	$10^{\circ}.0$	$10^{\circ}.6$	53.40	7.20	6.92	0.28
March 14.						
8.45 P.M.	$10^{\circ}.0$	$10^{\circ}.7$	53.16	7.24	6.92	0.32
March 15.						
10.00 A.M.	$10^{\circ}.0$	$10^{\circ}.8$	53.44	7.21	6.92	0.29
				7.22	6.92	0.30

Molecular osmotic pressure, 24.07.

Molecular gas pressure, 23.07.

Ratio of osmotic to gas pressure, 1.043.

Table VI.

0.3 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $36^{\circ}.7$; (2) at conclusion of Exp., $36^{\circ}.7$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.08 mm. Cell used, O. Resistance of membrane, 112,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 5.36. Time of setting up cell, 4.00 P.M., March 17, 1908.

Time,	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 19.						
5.00 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	53.79	7.15	6.92	0.23
10.00 P.M.	$10^{\circ}.1$	$10^{\circ}.9$	53.86	7.14	6.93	0.21
March 20.						
8.30 A.M.	$10^{\circ}.1$	$10^{\circ}.6$	53.65	7.17	6.93	0.24
10.30 P.M.	$10^{\circ}.0$	$10^{\circ}.8$	53.73	7.15	6.92	0.23
				7.15	6.93	0.22

Molecular osmotic pressure, 23.83.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.032.

Table VII.

0.4 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $48^{\circ}.1$; (2) at conclusion of Exp., $48^{\circ}.1$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.0 mm. Cell used, H. Resistance of membrane, 183,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.59; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.61. Time of setting up cell, 4.00 P.M., February 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 25.						
8.00 P.M.	$10^{\circ}.1$	$11^{\circ}.2$	40.86	9.53	9.24	0.29
Feb. 26.						
8.00 P.M.	$10^{\circ}.1$	$10^{\circ}.6$	40.98	9.52	9.24	0.28
10.00 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	40.85	9.54	9.23	0.31
				9.53	9.24	0.29

Molecular osmotic pressure, 23.83.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.031.

Table VIII.

0.4 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $48^{\circ}.1$; (2) at conclusion of Exp., $48^{\circ}.1$; loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.14 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections*: (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.55. Time of setting up cell, 4.30 P.M., February 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 25.						
8.30 A.M.	$10^{\circ}.1$	$100^{\circ}.75$	43.17	9.64	9.24	0.40
2.00 P.M.	$10^{\circ}.1$	$100^{\circ}.9$	43.37	9.59	9.24	0.35
5.00 P.M.	$10^{\circ}.05$	$110^{\circ}.0$	43.34	9.61	9.23	0.38
Feb. 26.						
10.00 P.M.	$10^{\circ}.0$	$100^{\circ}.9$	43.38	9.61	9.23	0.38
				9.61	9.24	0.38

Molecular osmotic pressure, 24.03.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.040.

Table IX.

0.5 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $59^{\circ}.0$; (2) at conclusion of Exp., $59^{\circ}.0$; loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.03 mm. Cell used, D. Resistance of membrane, 220,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 7.9. Time of setting up cell, 3.30 P.M., February 20, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 21.						
9.00 A.M.	$10^{\circ}.0$	$10^{\circ}.6$	35.13	11.95	11.54	0.41
5.00 P.M.	$10^{\circ}.0$	$11^{\circ}.0$	35.11	11.96	11.54	0.42
Feb. 22.						
9.00 A.M.	$10^{\circ}.0$	$10^{\circ}.4$	35.15	11.94	11.54	0.40
4.00 P.M.	$9^{\circ}.9$	$10^{\circ}.8$	35.04	11.98	11.54	0.44
				11.96	11.54	0.42

Molecular osmotic pressure, 23.92.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.036.

Table X.

0.5 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $58^{\circ}.7$; (2) at conclusion of Exp., $58^{\circ}.6$; loss, $0^{\circ}.1 = 0.17$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.64 mm. Cell used, G. Resistance of membrane, 139,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.88. Time of setting up cell, 4.00 P.M., March 17, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
March 18.						
10.00 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	35.00	12.00	11.54	0.46
March 19.						
8.00 P.M.	$10^{\circ}.0$	$10^{\circ}.8$	34.87	12.04	11.54	0.50
March 20.						
10.30 A.M.	$10^{\circ}.0$	$10^{\circ}.8$	34.89	12.04	11.54	0.50
				12.03	11.54	0.49

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.01.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.042.

Table XI.

0.6 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $69^{\circ}.2$; (2) at conclusion of Exp., $69^{\circ}.2$. loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.06 mm. Cell used, D. Resistance of membrane, 185,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.57. Time of setting up cell, 5.00 P.M., February 17, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	$10^{\circ}.1$	$10^{\circ}.4$	29.10	14.50	13.85	0.65
5.00 P.M.	$10^{\circ}.1$	$10^{\circ}.8$	29.02	14.55	13.85	0.70
Feb. 19.						
2.00 P.M.	$10^{\circ}.1$	$10^{\circ}.4$	29.11	14.53	13.85	0.68
				14.53	13.85	0.68

Molecular osmotic pressure, 24.22.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.049.

Table XII.

0.6 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $69^{\circ}.2$; (2) at conclusion of Exp., $69^{\circ}.2$; loss, 0° . *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.03 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections*: (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.8. Time of setting up cell, 5.00 P.M., February 17, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 18.						
9.00 A.M.	$10^{\circ}.1$	$10^{\circ}.4$	27.19	14.53	13.85	0.68
5.00 P.M.	$10^{\circ}.1$	$10^{\circ}.8$	27.11	14.57	13.85	0.72
Feb. 19.						
9.00 A.M.	$10^{\circ}.1$	$10^{\circ}.5$	27.20	14.53	13.85	0.68
2.00 P.M.	$10^{\circ}.1$	$10^{\circ}.4$	27.17	14.57	13.85	0.72
				14.55	13.85	0.70

Molecular osmotic pressure, 24.25.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.051.

Table XIII.

0.7 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $79^{\circ}.3$; (2) at conclusion of Exp., $79^{\circ}.2$; loss, $0^{\circ}.1 = 0.13$ per cent. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.16 mm. Cell used, G. Resistance of membrane, 373,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.61; (3) dilution, 0.01; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.38. Time of setting up cell, 4.00 P.M., January 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	$10^{\circ}.1$	$10^{\circ}.4$	23.19	17.10	16.16	0.94
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.7$	23.18	17.11	16.16	0.95
5.00 P.M.	$10^{\circ}.0$	$10^{\circ}.8$	23.23	17.07	16.16	0.91
				17.09	16.16	0.93

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.41.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.058.

Table XIV.

0.7 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $79^{\circ}.3$; (2) at conclusion of Exp., $79^{\circ}.3$; loss, 0° . *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.17 mm. Cell used, D. Resistance of membrane, 187,000. *Corrections*: (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.63; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.93. Time of setting up cell, 4.00 P.M., January 24, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 25.						
11.00 A.M.	$10^{\circ}.1$	$10^{\circ}.4$	24.85	17.07	16.16	0.91
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.7$	24.84	17.08	16.16	0.92
5.00 P.M.	$10^{\circ}.0$	$10^{\circ}.8$	24.82	17.10	16.16	0.94
				17.08	16.16	0.92

Molecular osmotic pressure, 24.40.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.057.

Table XV.

0.8 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $89^{\circ}.1$; (2) at conclusion of Exp., $88^{\circ}.9$; loss, $0^{\circ}.2 = 0.22$ per cent. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.28 mm. Cell used, G. Resistance of membrane, 186,000. *Corrections*: (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.62; (3) dilution, 0.03; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.96. Time of setting up cell, 5.00 P.M., January 29, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 30.						
9.00 P.M.	$9^{\circ}.9$	$10^{\circ}.8$	20.17	19.70	18.46	1.24
Jan. 31.						
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.6$	20.14	19.73	18.47	1.26
4.00 P.M.	$10^{\circ}.0$	$10^{\circ}.7$	20.19	19.68	18.47	1.21
				19.70	18.47	1.23

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.63.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.067.

Table XVI.

0.8 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $89^{\circ}.1$; at conclusion of Exp., $89^{\circ}.0$; loss, $0^{\circ}.1 = 0.11$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.25 mm. Cell used, D. Resistance of membrane, 184,000. *Corrections*: (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.02; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.46. Time of setting up cell, 5.00 P.M., January 29, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Jan. 30.						
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.6$	21.49	19.77	18.47	1.30
Jan. 31.						
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.6$	21.52	19.74	18.47	1.27
4.00 P.M.	$10^{\circ}.0$	$10^{\circ}.7$	21.52	19.75	18.47	1.28
				19.75	18.47	1.28

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.69.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.069.

Table XVII.

0.9 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $98^{\circ}.4$; (2) at conclusion of Exp., $98^{\circ}.0$; loss, $0^{\circ}.4 = 0.41$ per cent. *Manometer*: No. 6; volume of nitrogen, 405.34; displacement, 0.88 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.62; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.94. Time of setting up cell, 4.00 P.M., February 14, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 15.						
1.00 P.M.	10 [°] .0	11 [°] .4	17.91	22.24	20.77	1.47
11.00 P.M.	10 [°] .0	10 [°] .6	17.93	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10 [°] .0	10 [°] .4	17.93	22.20	20.77	1.43
				22.22	20.77	1.45

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.69.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.070.

Table XVIII.

0.9 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $98^{\circ}.4$; (2) at conclusion of Exp., $98^{\circ}.0$; loss, $0^{\circ}.4 = 0.41$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 0.68 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections*: (1) atmospheric pressure, 0.98; (2) liquids in manometer, 0.64; (3) dilution, 0.06; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.33. Time of setting up cell, 4.00 P.M., February 14, 1908.

Time.	Temperature.		Volume N ₂ .	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 15.						
11.30 P.M.	10 [°] .0	10 [°] .6	19.18	22.22	20.77	1.45
Feb. 16.						
10.00 A.M.	10 [°] .0	10 [°] .4	19.15	22.21	20.77	1.44
				22.22	20.77	1.45

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.69.

Molecular gas pressure, 23.08.

Ratio of osmotic to gas pressure, 1.070.

Table XIX.

1.0 Wt. normal solution. Experiment No. 1. *Rotation*: (1) original, $107^{\circ}.4$; (2) at conclusion of Exp., $106^{\circ}.8$; loss, $0^{\circ}.6 = 0.56$ per cent. *Manometer*: No. 13; volume of nitrogen, 432.84; displacement, 1.29 mm. Cell used, D. Resistance of membrane, 139,000. *Corrections*: (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.64; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.89. Time of setting up cell, 5.00 P.M., February 11, 1908.

Time.	Temperature.		Volume N ₂	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 12.						
8.00 P.M.	$10^{\circ}.3$	$11^{\circ}.6$	17.04	24.95	23.11	1.84
Feb. 13.						
9.00 A.M.	$10^{\circ}.2$	$10^{\circ}.5$	17.00	25.03	23.10	1.93
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	17.03	24.98	23.08	1.90
				24.99	23.10	1.89

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.99.

Molecular gas pressure, 23.10.

Ratio of osmotic to gas pressure, 1.081.

Table XX.

1.0 Wt. normal solution. Experiment No. 2. *Rotation*: (1) original, $107^{\circ}.4$; (2) at conclusion of Exp., $106^{\circ}.8$; loss, $0^{\circ}.6 = 0.56$ per cent. *Manometer*: No. 8; volume of nitrogen, 473.36; displacement, 0.85 mm. Cell used, G. Resistance of membrane, 278,000. *Corrections*: (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.66; (3) dilution, 0.09; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.24. Time of setting up cell, 5.00 P.M., February 11, 1908.

Time.	Temperature.		Volume N ₂	Pressure.		
	Solution.	Manometer.		Osmotic.	Gas.	Difference.
Feb. 12.						
11.30 P.M.	$10^{\circ}.2$	$10^{\circ}.4$	18.67	24.94	23.10	1.84
Feb. 13.						
9.00 A.M.	$10^{\circ}.2$	$10^{\circ}.5$	18.66	24.95	23.10	1.85
2.00 P.M.	$10^{\circ}.0$	$10^{\circ}.9$	18.68	24.92	23.08	1.84
				24.94	23.09	1.85

Loss in rotation corrected as inversion.

Molecular osmotic pressure, 24.94.

Molecular gas pressure, 23.09.

Ratio of osmotic to gas pressure, 1.080.

Table XXI. Series II.

Summary of Results.

Weight-normal concentration.	No. of experiment.	Temperature of solution.	Per cent. loss in rotation.	Osmotic pressures.			Theoretical gas pressure.
				Inversion.	One half dilution.	No inversion, no dilution.	
0.1	1	10° 0	0.00	2.43	2.43	2.43	2.31
0.1	2	10° 0	0.00	2.44	2.44	2.44	2.31
0.2	1	10° 0	0.00	4.81	4.81	4.81	4.62
0.2	2	10° 0	0.00	4.83	4.83	4.83	4.62
0.3	1	10° 0	0.00	7.22	7.22	7.22	6.92
0.3	2	10° 1	0.00	7.15	7.15	7.15	6.93
0.4	1	10° 1	0.00	9.53	9.53	9.53	9.24
0.4	2	10° 1	0.00	9.61	9.61	9.61	9.24
0.5	1	10° 0	0.00	11.96	11.96	11.96	11.54
0.5	2	10° 0	0.17	12.03	12.05	12.04	11.54
0.6	1	10° 1	0.00	14.53	14.53	14.53	13.85
0.6	2	10° 1	0.00	14.55	14.55	14.55	13.85
0.7	1	10° 0	0.13	17.09	17.11	17.10	16.16
0.7	2	10° 0	0.00	17.08	17.08	17.08	16.16
0.8	1	10° 0	0.22	19.70	19.75	19.73	18.47
0.8	2	10° 0	0.11	19.75	19.78	19.77	18.47
0.9	1	10° 0	0.41	22.22	22.33	22.28	20.77
0.9	2	10° 0	0.41	22.22	22.33	22.28	20.77
1.0	1	10° 2	0.56	24.99	25.16	25.08	23.10
1.0	2	10° 1	0.56	24.94	25.11	25.03	23.09

Table XXII. Series II.
Summary of Results.—Mean Values.

Weight-normal concentration.	Temperature of solution.	Per cent. loss in rotation.	Osmotic pressures.			Theoretical gas pressure.
			Inversion.	One half dilution.	No inversion, no dilution.	
0.1	10°.0	0.00	2.44	2.44	2.44	2.31
0.2	10°.0	0.00	4.82	4.82	4.82	4.62
0.3	10°.1	0.00	7.19	7.19	7.19	6.93
0.4	10°.1	0.00	9.57	9.57	9.57	9.24
0.5	10°.0	0.09	12.00	12.01	12.00	11.54
0.6	10°.1	0.00	14.54	14.54	14.54	13.85
0.7	10°.0	0.07	17.09	17.10	17.09	16.16
0.8	10°.0	0.17	19.73	19.77	19.75	18.47
0.9	10°.0	0.41	22.22	22.33	22.28	20.77
1.0	10°.1	0.56	24.97	25.14	25.06	23.09

Av. = 10°.0 Av. = 0.13

Table XXIII. shows the differences between osmotic and gas pressures derived from Table XXII., and also the differences when no correction is made for loss in rotation.

*Table XXIII.—Differences between Osmotic and Gas Pressure.
Series II.*

Weight-normal concentration.	If all loss in rotation is ascribed to inversion.	If one half the loss in rotation is ascribed to dilution.	If all loss in rotation is ascribed to subsequent dilution.
0.1	0.13	0.13	0.13
0.2	0.20	0.20	0.20
0.3	0.26	0.26	0.26
0.4	0.33	0.33	0.33
0.5	0.46	0.47	0.46
0.6	0.69	0.69	0.69
0.7	0.93	0.94	0.93
0.8	1.26	1.30	1.28
0.9	1.45	1.56	1.51
1.0	1.87	2.04	1.96

As in Series I., Table XXIV. contains the ratios of the molecular osmotic pressures to the molecular gas pressures, including their ratios if all the dilution is subsequent to the measurement of pressure.

Table XXIV.—Ratios of Molecular Osmotic Pressure to Molecular Gas Pressure.

Series II.

Weight-normal concentration.	If all loss in rotation is ascribed to inversion.	If one half the loss in rotation is ascribed to dilution.	If all loss in rotation is ascribed to subsequent dilution.
0.1	1.053	1.053	1.053
0.2	1.043	1.043	1.043
0.3	1.038	1.038	1.038
0.4	1.036	1.036	1.036
0.5	1.039	1.040	1.039
0.6	1.050	1.050	1.050
0.7	1.058	1.058	1.058
0.8	1.068	1.070	1.069
0.9	1.070	1.075	1.073
1.0	1.081	1.089	1.085

It has been stated that Series II. has shown that most of the dilution takes place when the cell is being opened.

It may be asked then, Why should any correction for loss in rotation be made, since any dilution arising after the measurement has been made, does not affect the osmotic pressure? In other words, why should not the actually observed osmotic pressure be the true one?

Some years ago Morse and Frazer tested all their sugar solutions, both before and after a measurement had been made,¹ to see if they could detect inversion. Fehling's solution gave negative results with the lower concentrations. In the case of the higher concentrations, however, 0.5 to 1.0 normal, inversion was detected, but it was never sufficient in quantity to justify a correction of more than 0.05 of an atmosphere. At this time they were inclined to believe that it was safe to attribute most of the loss in rotation to inversion.

Somewhat later² they were of the opinion that most of the loss in rotation could be ascribed to dilution. With improved methods for opening the cells, the loss in rotation decreased rapidly from 2.8 per cent in the second series of measurements in the vicinity of 20°, to 0.93 per cent as shown in Series I. at 10°.

If the loss in rotation had been due to any great extent to inversion, it is difficult to see why there should have been any marked decrease in the loss in rotation. That is, the amounts of inversion for any one concentration in the different series should have been fairly constant if the pressures actually obtained for that concentration agree, as they have done.

With the use of the hypodermic needle the average loss in rotation of the solutions was reduced to 0.13 per cent in Series II. at 10°.

For the sake of comparison the following table is given showing the losses in rotation of Series I. and II., the former being the last series in which the cells were opened by the old method.³ The second column in both series, that is, the loss in rotation calculated in atmospheres, is based upon the assumption that *all* loss in rotation is due to inversion.

¹ Am. Chem. J., **34**, 31.

² *Ibid.*, **36**, 42, 51; **37**, 463; **38**, 199.

³ *Ibid.*, **34**, 20.

Table XXV.—Loss in Rotation.

Series I.

Weight-normal concentration.	Loss in rotation. Per cent.	Loss in rotation. Atmospheres.
0.1	0.39	0.005
0.2	0.80	0.02
0.3	0.76	0.04
0.4	0.83	0.06
0.5	1.13	0.10
0.6	1.15	0.07
0.7	1.26	0.15
0.8	...	...
0.9	...	...
1.0	1.12	0.19

Av. = 0.93

Series II.

Weight-normal concentration.	Loss in rotation. Per cent.	Loss in rotation. Atmospheres.
0.1	0.00	0.00
0.2	0.00	0.00
0.3	0.00	0.00
0.4	0.00	0.00
0.5	0.09	0.005
0.6	0.00	0.00
0.7	0.07	0.005
0.8	0.17	0.025
0.9	0.41	0.06
1.0	0.56	0.09

Av. = 0.13

It will be noticed that in the measurements in Series II. at 10°, with the exception of the 0.5 normal, there is no loss in rotation until the 0.7 normal is reached. It may be noted here that, both in the case of the 0.5 normal and of the 0.7 normal, all the loss in rotation occurred in one of the determinations, there having been no loss in the duplicates.

Since there was no loss in rotation from the 0.1 to the 0.5 normal, and since the cells from the 0.5 normal on, were closed in the same way as for the lower concentrations, it

appears probable that the small loss observed in the 0.5, 0.7, 0.8, 0.9 normal, and the normal solutions, is to be ascribed in part, at least, to inversion, and the results in Tables I. to XX., inclusive, have been so corrected.

In Tables XXI. to XXIV., inclusive, the results have been presented in three ways: (1) as corrected for inversion; (2) as corrected if one half the loss in rotation is ascribed to dilution; and (3) without any correction for loss in rotation. It is believed that the results without any correction, whatsoever, are the nearest approximations to the true osmotic pressures of the solutions.

CONCORDANCE OF THE RESULTS.

By referring to Table XXI., it will be noticed that the differences between duplicate determinations of the individual concentrations is in all cases confined to the second decimal place. This is a degree of concordance which has not been reached in any of the earlier measurements of the osmotic pressure of cane sugar solutions, and is due to the improvements in methods which have already been discussed.

MOLECULAR RATIOS.

Notwithstanding the belief that the actually observed osmotic pressures are more accurate than those corrected for loss in rotation, the pressures corrected for inversion and for half dilution give practically the same ratios of molecular osmotic pressure to molecular gas pressure as the uncorrected pressures. This concordance is due to the small loss in rotation. This close agreement in the ratios, whatever the method of correcting the results, will be seen in Table XXIV.

Even if half of the loss in rotation should be ascribed to inversion, the largest difference in the molecular ratios of osmotic to gas pressure would be only 0.004 in the case of the normal concentration, while, up to the 0.8 normal, the two ratios thus calculated would be identical.

By referring to Table XXIV., it will be observed that in a general way up to the 0.6 normal the excess of osmotic over

gas pressure is about 4 per cent., while, from that point on, the excess of osmotic over gas pressure increases until in the normal solution it reaches about 8.5 per cent. This is quite analogous to relations observed in measurements at other temperatures, also to those observed among the freezing points of cane sugar solutions.

The molecular ratios are all lower than those obtained in the two previous series at lower temperatures—those in the vicinity of 0° ¹ and 4° .² There is the usual minimum at the 0.4 normal likewise observed at this same concentration in the vicinity of 0° and 20° .³

The uncorrected osmotic pressures, however, are higher in Series II. at 10° , than in the vicinity of 0° and, with a few exceptions in the lower concentrations, than in the vicinity of 4° . This same fact appears in the series at 15° .⁴ These results would seem to dispose of the question of a minimum in the osmotic pressure of cane sugar solutions between 0° and 20° .

TEMPERATURE COEFFICIENT.

Evidences of a decided temperature coefficient in the osmotic pressure of cane sugar solutions will be seen when one compares Series III., IV. and V. in Table XXVI. The three columns of the different series contain the osmotic pressures without any correction for loss in rotation. The reason for thus calculating the pressures need not be repeated.

It will be observed that the total pressures of the individual series increase from Series III. to Series IV. and from Series IV. to Series V. The rise from Series III. to IV. is 0.97 atmosphere while that from Series IV. to V. is 2.07 atmospheres.

¹ Am. Chem. J., **38**, 207.

² *Ibid.*, **38**, 207.

³ *Ibid.*, **38**, 207.

⁴ *Ibid.*, 40.

Table XXVI.—A Comparison of Series V. with Series III. and IV.

	Series III.	Series IV.	Series V.
Concentration.	Pressures. 0°	Pressures. 4°-5°	Pressures. 10°
0.1	2.42	2.40	2.44
0.2	4.79	4.75	4.82
0.3	7.11	7.07	7.19
0.4	9.35	9.43	9.58
0.5	11.75	11.82	12.00
0.6	14.12	14.43	14.54
0.7	16.68	16.79	17.09
0.8	19.15	19.31	19.75
0.9	21.89	22.15	22.28
1.0	24.45	24.53	25.06
Total pressure	131.71	132.68	134.75
Difference		0.97	2.07
Mean molecular osmotic pressure	23.95	24.12	24.50
Difference		0.17	0.38
Per cent		0.71	1.58
Mean molecular gas pressure	22.29	22.65	23.09
Difference		0.36	0.44
Per cent		1.62	1.94

The mean molecular osmotic pressures are obtained by dividing the total pressures of the several series by the sum of the concentration units (5.5).

The mean molecular osmotic pressures thus obtained for the three series in the table rise from 23.95 atmospheres (Series III.) to 24.50 atmospheres (Series V.). The rise is about twice as great (0.38 atmosphere) from 4°-5° to 10°, as from 0° to 4°-5° (0.17 atmosphere). About the same rise takes place from 10° to 15°¹ as from 4°-5° to 10°. Thus with rise in temperature there is an increase in the mean molecular osmotic pressure.

The rise in mean molecular gas pressure from 0° to 4°-5° is 0.36 atmosphere while that from 4°-5° to 10° is 0.44 atmosphere. This fact shows that, while the rise in mean molecular gas pressure from 0° to 4°-5° is 1.62 per cent

¹ Am. Chem. J., 40,

and that from 4° - 5° to 10° is 1.94 per cent, an increase of 0.32 per cent, the rise in mean molecular osmotic pressure from 0° to 4° - 5° is 0.71 per cent, and from 4° - 5° to 10° is 1.58 per cent, an increase of 0.87 per cent. That is, the mean molecular osmotic pressure from 0° to 4° - 5° appears to increase only 0.44 as fast as the mean molecular gas pressure, while from 4° - 5° to 10° it increases 0.81 as fast as the mean molecular gas pressure.

BIOGRAPHY.

The writer was born in Baltimore, Md., February 18, 1883. He received his early education in the public schools of that city and the degree of A.B. from Johns Hopkins University in 1905.

